Second Semiannual Technical Report

(NASA Grant NsG-337)

CHEMICAL REACTIVITY OF HYDROGEN, NITROGEN AND OXYGEN ATOMS AT TEMPERATURES BELOW 100° K.

UNPUBLISHED PRELIMINARY DATA

by

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PRINCIPLE INVESTIGATOR

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Project A-661

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A. Introduction

The objectives of this program are three:

1. To study quantitatively the reactivity of hydrogen, nitrogen and oxygen atoms with low molecular weight compounds of carbon, hydrogen, oxygen and nitrogen at temperatures below 100° K.

2. To investigate fractional freezing, adsorption and absorption as possible purification techniques for the separation of the unusual product mixtures that are obtained from the above cryochemical reactions.

3. To study the subsequent chemical behavior of these low temperature reaction products as a function of temperature during warm-up to room temperature.

Particular emphasis is to be placed upon the isolation, as well as the identification, of the often unusual products of such reactions, many of which will exist only so long as the low temperature is maintained. The macroscopic chemical and physical behavior of these hopefully pure products are also to be studied, both at the lowest temperatures and as a function of temperature during warm-up to room temperature. The definitive chemical studies that are to be performed are made possible by a unique mass spectrometer analytical technique which permits cold, in situ analysis of the reactive low temperature materials without prior warm-up.

It is now generally realized that any real understanding of certain astronomical objects, e.g., comets, must rest in large part upon low temperature chemistry (see article by Donn in (1)).

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[1] Bass and Broida, editors, Formation and Trapping of Free Radicals, Academic Press, New York, 1960.

B. Background Information

The broadest investigations of low temperature chemical reactivity were those of Geib and Harteck who made a qualitative study of the reactivity of H, N, O and other atoms with a variety of reactants in a reactor cooled in liquid air.[2,3,4] These observations were made in the early 1930's and all conclusions from them are tentative and based only on the qualitative appearance and behavior of the low temperature substances. However, the fact that unusual and energetic processes do actually occur under such conditions was clearly demonstrated. It is interesting that during a recent visit to our laboratory, Dr. Harteck remarked that at the time he and Geib did this work, only the Indian astrophysicist, Chandrasakhar, was interested in the results. Several examples will serve to illustrate not only the nature of these early experiments, but also the particular point of view that characterizes this research program.

A very unstable compound that has been tentatively identified as HNO, or perhaps $(HNO)_n$, is made by reacting hydrogen atoms with nitric oxide at liquid air temperatures.[3,5] A light yellow transparent film may be frozen onto the walls of a reactor that is immersed in liquid air when a stream of hydrogen atoms from a discharge tube meets a stream of gaseous NO in the center of the reactor (see, e.g., Geib and Harteck[6]). The product is stable at liquid air

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[2] Geib, and Harteck, Ber. 66, 1815 (1933).

[3] Geib, and Harteck, Trans. Faraday Soc. 30, 131 (1934).

[4] Schenk, and Jablonowski, Z. anorg. u. allgem. Chem. 244, 397 (1940).

[5] Harteck, Ber. 66, 423 (1933).

[6] Geib, and Harteck, Ber. 65, 1551 (1932).

temperatures, but on rapid warming the film will explode. An explosive substance that may also be HNO may be made by reacting NH_3 and oxygen atoms in a similar experimental arrangement.[7]

It has also been observed that hydrogen atoms will react with $(CN)_2$ at low temperatures to produce a dark red, but presently uncharacterized product. The product from a similar reaction of hydrogen atoms with HCN will decompose on warming. Oxygen atoms will react with unsaturated hydrocarbons such as ethylene and acetylene to produce intensely colored products most of which decompose with heavy frothing on warming to still rather low temperatures, i.e., 160°-180° K. A rather broad literature review of these and many other experiments in cryochemistry containing over 200 references has been prepared by McGee and Martin.[8] It is our objective to restudy and to expand upon some of these much earlier observations of chemical reactivity.

Chemical analysis of the cold reaction mixtures without prior warm-up is a necessity. Studies by conventional means at room temperature are inadequate because of the unknown reactions that may occur during the warm-up. Indeed, the observation of the chemical behavior of the cold substances is the real essence of the experiment, and clearly such studies must be largely based upon accurate low temperature chemical analysis.

The present availability of physical analytical instruments which may, in principle, be used at cryogenic temperatures has provided a great impetus to chemical research at these temperatures. The recent engineering developments permitting the ready and inexpensive availability of cryogenic refrig-

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[7] Geib, Naturwissenschaften 15, 44 (1936).

[8] McGee and Martin, Cryogenics 2, 257 (1962).

erants have had a comparable catalyzing influence. Of the many instruments that may be used for low temperature analysis, we selected the Bendix time-of-flight mass spectrometer. There were three basic reasons for this choice. First, the output data are simple and can be easily understood by persons not expert in specialized areas of modern physics. The reverse of this is true, for example, for the nuclear magnetic resonance and electron spin resonance spectrometers, as well as for optical spectroscopy. Secondly, the mass spectrometer will permit identification of all species and not just free radicals as does the electron spin resonance spectrometer. And thirdly, the Bendix instrument is designed such that it was a relatively simple problem to modify and adapt it for the introduction of a cryogenic sample. In doing this, the sample gas must not suffer collisions with any other gaseous molecules or with any surface that is not at ambient temperature prior to its fragmentation and ionization. Here ambient temperature may be as low as 4.2° K. The required design modifications were developed with consultation from the Bendix Corporation engineering and research staff and allow for the use of several inlet arrangements, each of which has its particular advantages and disadvantages. The design currently in use is discussed later in this report.

Mass spectrometer analysis of the vapor over the low temperature substances during controlled warm-up should also give information on the chemical processes that usually occur, e.g., rearrangements, dissociations, etc. Our studies utilize both a "quenched diffusion flame" type reactor similar to that of Geib and Harteck[6] and a gas-liquid and a gas-solid reactor that has been designed somewhat like the atomic hydrogen and liquid ozone reactor of Kobozev.[9] Such

[9] Kobozev, et al., Zhur. Fiz. Khim. 31, 1943 (1957).

multiple studies are necessary if one is to answer questions of detailed chemical behavior. For example, the question of whether one is quenching a gas phase reaction which may be occurring at several hundreds of degrees or observing a true low temperature reactivity is often asked, but heretofore been seldom answered.

During the three year course of this program, the particular choice of reactant molecules will be based on, (1) the cumulative experience up to that particular time, and (2) on conferences with knowledgable persons within NASA as to which species are of most interest from the point of view of cosmic chemistry.

II. CURRENT STATUS OF RESEARCH

A. Ionization and Appearance Potential Measurements

The experimental determination of ionization potentials is important for the numbers are useful in thermochemistry, in kinetics, and other areas of chemistry and chemical physics. More specifically, for the case of the unusual chemical behavior at very low temperatures that is of concern here, the data may be applied to identification problems, to molecular structure problems and to unusual chemical kinetic problems. Let us discuss this area under the four separate headings of (1) equipment, (2) identification, (3) structure, and (4) kinetics.

1. Equipment

Our procedure for the experimental determination of the appearance potentials closely follows that of Hamill and Melton[10] and employs the Fox retarding potential difference (RPD) method.[11] This method is well suited for use with the Bendix T-O-F Mass Spectrometer and is generally thought to be the most accurate method available for the measurement of appearance potentials by electron impact techniques.

The mass spectrometer was modified to permit use of the RPD procedure by the installation of a five-grid electron gun (Bendix Part No. MPL-101) and the construction of the necessary circuitry to apply the proper potential to each grid. These modifications permit the study of the effect of a stream of electrons of a very narrow energy range.

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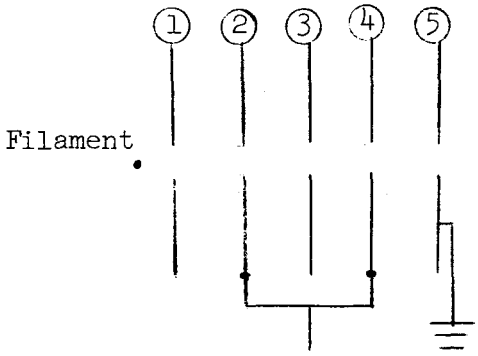
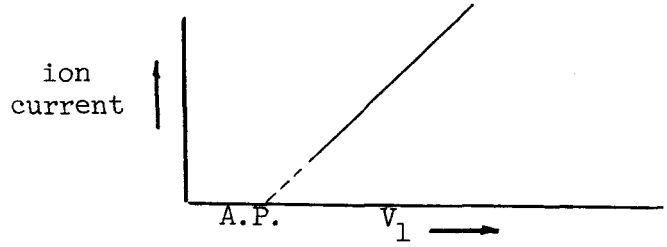
[10] Hamill and Melton, J. Chem. Phys., to be published.

[11] Fox, et al, Rev. Sci. Instruments 26, 1101 (1955).

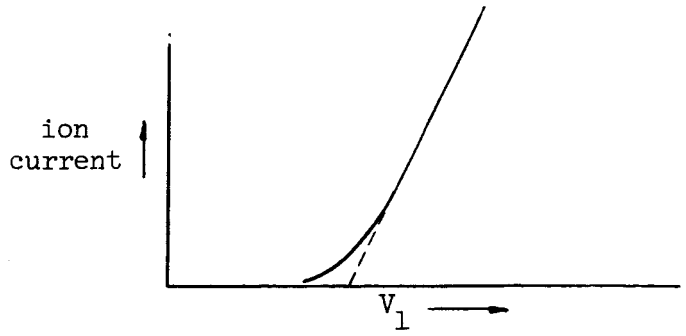


Grid	Potential
1. Control Grid	Control Pulse
2. Retard Shield	Filament + 2.0v
3. Retarding Grid	Filament - 0.2 to-0.4v
4. Retard Shield	Filament + 2.0v
5. Ground	

The filament and grids 1 and 5 are used in the normal manner (i.e., as for a two grid electron gun) and grids 2 and 4 serve only as shields for the retarding grid, and are electrically connected together. This means only two additional feed throughs are required on the source in addition to those for normal operation, i.e., 15 instead of 13. The filament is maintained V_1 volts negative with respect to the ionization chamber. If none of the electrons were produced with an initial kinetic energy, the energy of the electrons in the ionization region would be determined solely by V_1 and the determination of appearance potentials would be straight forward. The ion current for the species of interest could be recorded at successively lower values of V_1. A plot of ion current vs. V_1 should cross the V_1 axis at the appearance potential.

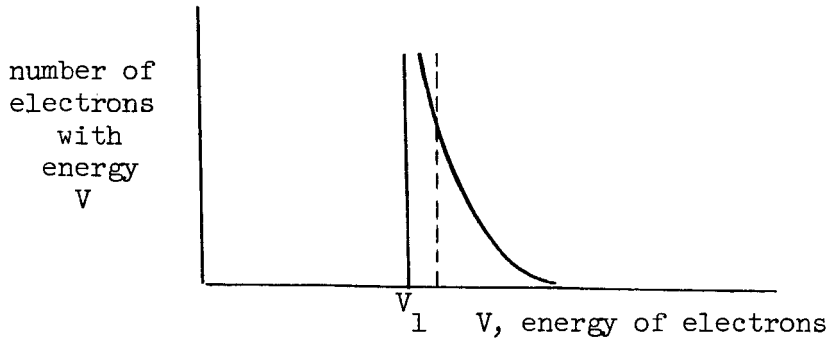


In practice, the data yield curves which tail off near the appearance potential. This effect is due to the initial kinetic energy of the electrons. Even when V_1 is somewhat less than the appearance potential, the more energetic electrons will be able to produce ionization.

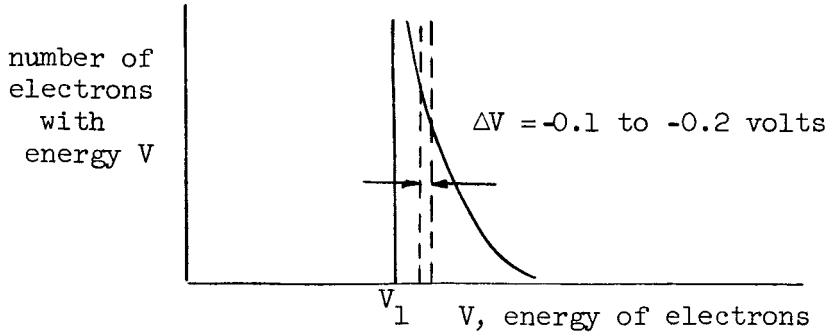


Extrapolation of the linear portion of this curve yields fairly good appearance potentials but a much more satisfactory procedure would be to examine the effect of an almost mono-energetic beam of electrons. This is what is done in the Fox RPD method.

By applying a small bias (negative with respect to the filament) to grid 3 we can cut off the part of the electron beam of lowest energy. This energy cutoff is very sharp.



If we now change this bias by a small value, ΔV, we cut out a slice of electrons of very small energy spread.



The change in the ion current, Δi , due to this change in the electron beam will, of course, represent the ions which were produced by the electrons in this narrow energy band. If the electron energy is below the appearance potential of the species under investigation, there will be no change in ion current due to the small change in bias. By recording Δi corresponding to ΔV at a series of values of electron energy, we can accurately locate the appearance potential. An actual Visicorder trace from a typical experiment (looking at the N_2^+ ion) is reproduced in Figure 1. The change in ion current due to the retarding potential can be clearly seen for each value of electron energy above the uncorrected appearance potential.

The bias is returned to its original value after being retarded to insure that there has been no drift in the ion current. At each electron energy the retarding potential must be changed by exactly the same amount. A plot of Δi vs. electron energy will intercept the energy axis at the uncorrected appearance potential of the species. Because of contact potentials and other instrumental factors, this will not correspond to the actual appearance potential but the shift should be constant for all molecules. Therefore, it is only necessary to study one molecule whose appearance potential is well known in order to fix the value of this correction. Actually, we have studied several ions of known appearance potential to insure the correct value of this correction.

The values of the various potentials are read on a Cimron Series 6000 digital voltmeter which is accurate to 0.01 volts up to 99.99 volts and to 0.001 volts up to 9.999 volts (as certified by the manufacturer and verified potentiometrically in this laboratory). However, because of fluctuations in the ion current output we can only expect to attain 0.1 volt accuracy in our final results.

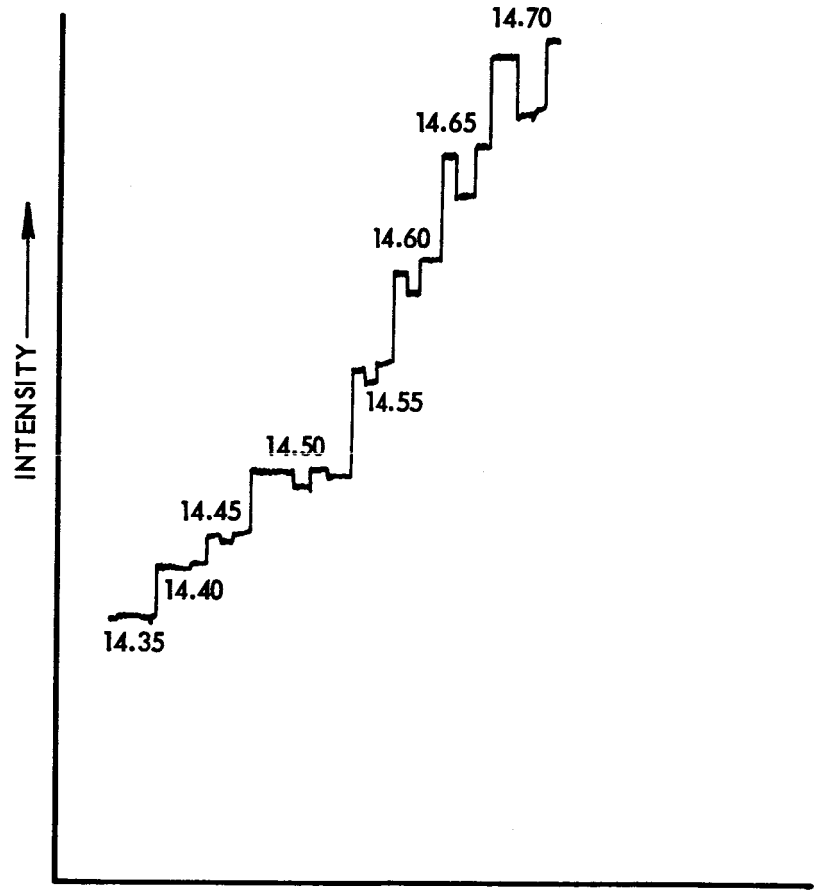


Figure 1. N_2^+ Ion Current Showing Effect of Retarding Grid. Indicated Energies are Uncorrected.

The appearance potentials of the ions N_2^+, O_2^+, and N^+ have been measured and, although the spectrometer output has been somewhat erratic, the results indicate that we may predict the differences in appearance potentials to within $\pm$ 0.1 volt for ions whose appearance potentials differ by only a few electron volts.

	$IP(N_2) - IP(O_2)$
Present work	3.35 ± 0.1
Spectroscopic	3.32[12]
	3.0 [13]
Electron Impact Methods	3.4 [14]
	3.5 [15]

For appearance potentials which differ by as much as 10 electron volts we can still measure these differences to within $\pm$ 0.3 ev.

2. Identification

Positive identification of labile species is, of course, basic to this entire research program. If we are concerned, for example, with mass spectrometric proof of the presence of HNO from a cryogenic reactor, it is necessary that we differentiate between HNO^+ ions from HNO as opposed to HNO^+

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12 Modern Mass Spectrometry, Barnard, The Institute of Physics (London), 1953.

13 Handbook of Chemistry and Physics, 40th Edition, Chemical Rubber Company, 1958.

14 Magstrum and Tate, Phys. Rev. 59, 354 (1941).

15 Field and Franklin, Electron Impact Phenomena, Academic Press, New York, 1957.

ions that may arise from any other species that may possibly be present, say from HNO_2. The problem here is not quite equivalent to that of free radical identification by fast inlet mass spectrometry that was originated by Eltenton,[16] for here we do not admit that the species of interest (say HNO) is unstable or transitory in its existence if it is kept cold. The inlet system that has been devised and which is discussed subsequently has, however, been designed as a high speed inlet because we wish to study the kinetics of reactions into which the unusual species may enter.

If we think of the above example as typical of the identifications that are demanded, let us run an ionization efficiency curve using the Fox RPD technique on mass 31, (HNO^+). If the HNO^+ is coming from HNO, its appearance potential will be less than that from HNO_2 by D(HNO-O), and if this is as much as a few tenths of an electron volt it will be detectable by our present arrangement. It will also be possible to say in what ratio HNO and other species may be present in a mixture. One would need an independent earlier calibration on species that appear with the HNO.

We have not yet made any identifications of such low temperature systems. The exact data for definitive arguments will likely be specific for each substance, but they will all follow such reasoning as that outlined above.

3. Structure

Information is desired on the structure of the unusual molecules that are expected to result from studies of the reactions of hydrogen,

[16] Eltenton, J. Chem. Phys. 10, 403 (1942).

nitrogen and oxygen atoms with simple molecules at cryogenic temperatures.* Using the mass spectrometer we can determine the ionization energy from which we can deduce bond energies. Also, from the fragmentation pattern, one can make deductions about which atoms are bonded to which in the molecule. For example, if from HNO one sees NH^+ but not OH^+, it seems reasonable that the H atom must be on the N atom and not on the O atom.

The bond dissociation energies may be developed in two ways.[17] If an ion X^+ is known to arise by the process:

$$XY + e \rightarrow X^+ + Y + 2e \ ,$$

then the appearance potential of the X^+ ion is given by,

$$V(X^+) = D(X\text{-}Y) + I(X) + KE + EE \ .$$

D(X-Y) is the dissociation energy of the X-Y bond; I(X) is the ionization energy of X ; KE and EE are the excess kinetic and excitation energy respectively of any of the fragments leaving the point of impact. Notice that X and Y need not be only atoms. We usually set the latter two terms equal to zero, and hence one needs only to measure V and I to deduce D(X-Y).

If the ionization energy of X is not available, then it is possible to use thermochemical data together with two values of V to deduce D. For example, let us determine the appearance potential, V , of the species X^+

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* As is mentioned in Chapter III, there is already a strong interest by workers in our Diffraction Laboratory in studying the structure of some of these unusual molecules.

17 Margrave, J. Chem. Phys. 24, 475 (1956).

from XY and from XZ. For the reaction,

$$XY + ZW \rightarrow XZ + YW$$

which has a heat evolution of ΔH_r as gotten from the heats of formation of the four separate species. The individual heats of formation may be written,

$$X + Y \rightarrow X\text{-}Y + D(X\text{-}Y)$$

when we arbitrarily set the zero of enthalpy at X , Y , etc., and which may be equivalently written,

$$X + Y \rightarrow X\text{-}Y + V(XY) - I(X) \ .$$

An enthalpy balance on the reaction as written above then becomes,

$$V(XY) - I(X) + D(Z\text{-}W) = V(XZ) - I(X) + D(YW) + \Delta H_r$$

or,

$$D(ZW) = V(XZ) - V(XY) + D(YW) + \Delta H_r$$

Note that for an exothermic reaction ΔH_r is a negative member. If we measure the V's and if D and ΔH_r are known from thermochemical data, we can evaluate the unknown bond energy D(ZW). This technique has been extensively used by Stevenson in work with various hydrocarbons.[18]

Although we have not yet applied either of these techniques to a low temperature substance of the sort in which we are here concerned, we have

[18] Stevenson, Discussions Faraday Soc. 10, 35 (1951).

recently obtained some interesting information on CHI_2 from the pyrolysis of CHI_3. In studying the pyrolysis products of CHI_3 by the fast inlet techniques described previously,[19] it was found that the peak height of CHI_2^+ increased relative to the peak height of CHI_3^+ as the furnace temperature was increased. This increase is marked as may be seen from the following table.

Temperature	$\frac{\text{Peak Hgt. of } CHI_2^+}{\text{Peak Hgt. of } CHI_3^+}$
60° C	3.25
100° C	3.62
144° C	3.72
300° C	4.35

These data indicated that the hot gases contained a significant fraction of the CHI_2 radical. If we assume that the ionization efficiencies of the CHI_3 and CHI_2 molecules are nearly equal, these results imply that approximately 13 per cent of the iodoform is dissociated at 300° C. If the ionization efficiency of the CHI_2 radical is larger by a factor of ten, only about 1.3 per cent of CHI_3 would be dissociated at this temperature.

This large current of CHI_2^+ ions due to CHI_2 radicals allowed the determination of the ionization potential of CHI_2 without great difficulty. However, the CHI_2 radicals were present to a small extent in the CHI_3 vapor at the lowest temperature at which a reasonable spectrum of iodoform could be obtained. Therefore, the measurement of the appearance potential of the

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[19] Final Report on NsG-123-61, Chemical Syntheses Requiring Cryogenic Temperatures as Preparative Techniques for Highly Endothermic Chemical Species, Georgia Tech Research Institute, August, 1963.

CHI_2^+ ion from CHI_3 could be made only with much less precision. A plot of Δi vs. electron energy for the CHI_2^+ ion is shown in Figure 2. The ionization potential of CHI_2^+ as formed from CHI_3 is less precise since it must be determined from the point at which this curve began to depart from a straight line. From Figure 2 it can be seen that this appearance potential is approximately 11.5 volts.

These potentials can be used to estimate the energy of the CHI_2-I bond.

$$D(CHI_2\text{-}I) = AP(CHI_2^+) - IP(CHI_2)$$

$$= 11.5 - 10.0 \text{ ev}$$

$$= 1.5 \text{ ev}$$

This corresponds to a bond energy of about 35 kcal/mole which seems to be a reasonable value.

The ionization potential of CHI_3 was found to be 9.45 ± 0.1 ev. This corresponds closely to the ionization potential of I_2, CH_3I and other iodine compounds and, hence, we can deduce that ionization is from the non-bonding electron pairs on the iodine atom.

4. Kinetics

The fast inlet mass spectrometer is a powerful tool for the study of chemical kinetics as was first demonstrated by Eltenton[16] and subsequently by Hipple and Stevenson,[20] by Lossing and coworkers,[21] and by others. The

[20] Stevenson and Hipple, Phys. Rev. 63, 121 (1943).

[21] Lossing and Tickner, J. Chem. Phys. 20, 207 (1952).

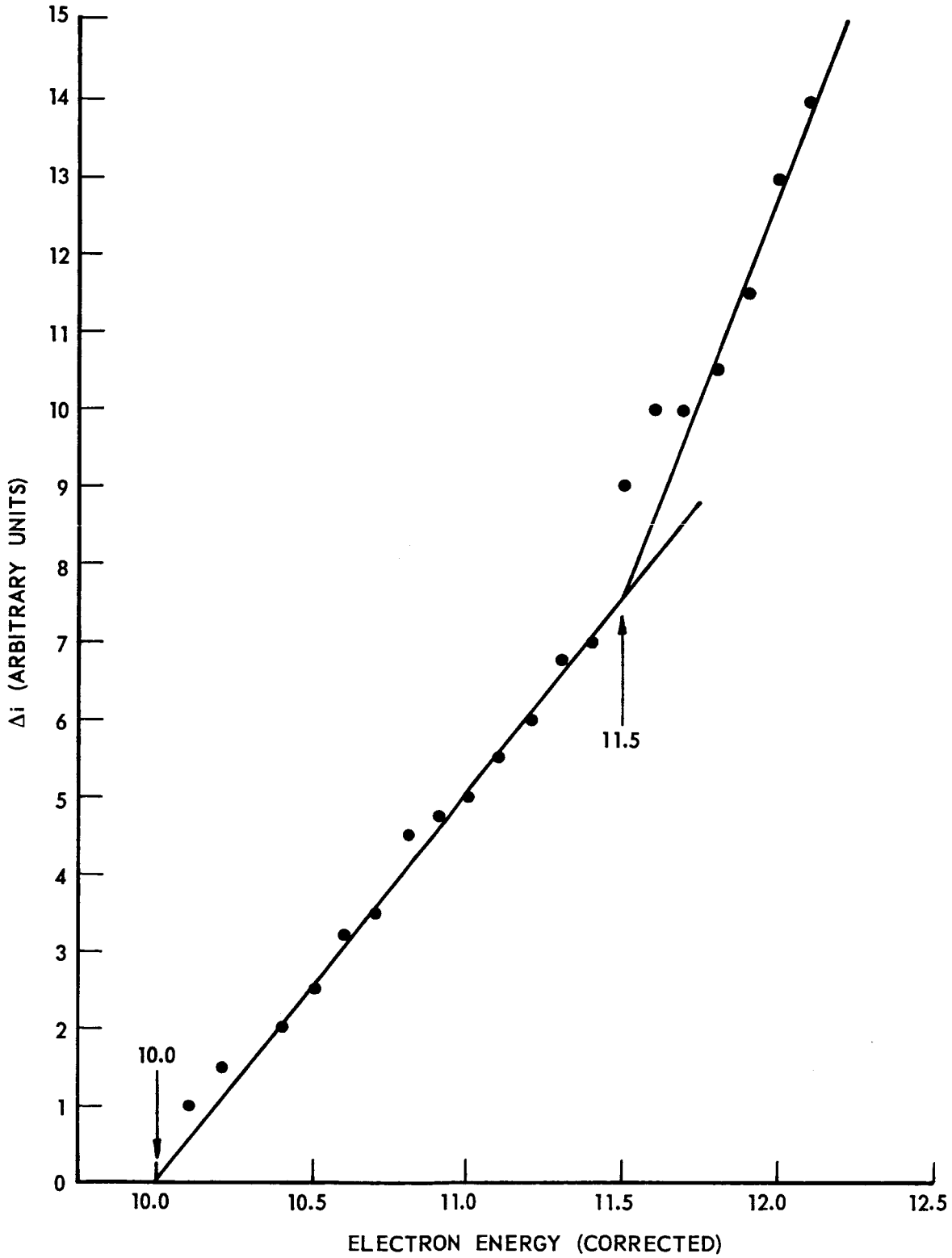

Figure 2. RPD Δi Ion Current as a Function of Electron Energy for the Ion CHI_2^+.

currently most sophisticated apparatus for studies of kinetics by mass spectrometry is that of Foner and Hudson.[22] A particularly significant study for our own program was that of Bradley and Kistiakowsky[23] who used a Bendix time-of-flight spectrometer to study kinetics in shock heated gases.

In our cryogenic inlet system that is briefly described in the following section of this report, the ionizing electron beam of the spectrometer makes grazing trangential contact with an outlet port in the cold reactor itself. The design is such that the vapor from the cold reactor is ionized before any collisions of higher energy than cryogenic ambient may occur. Initial experiments with this arrangement using the interesting substance O_3F_2 are now in progress in this laboratory, but no results worth discussing have as yet been obtained. The substance decomposes into O_2F_2 and O_2 beginning at a significant rate near 90° K.* We should be able to follow this reaction nicely, hopefully also getting sufficient data to make reasonable arguments about the mechanism of the decomposition.

These remarks point up an interesting analogy of this work to the rather highly developed fast inlet work of Eltenton, Lossing and others. Whereas these workers are producing the labile species by some high energy process such as a pyrolysis or a flash photolysis, or whatever; we produce the labile species by slightly warming a highly reactive substance at cryogenic temperatures. The ideas are quite analogous but merely separated by an order of magnitude or so in temperature.

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[22] Foner and Hudson, J. Chem. Phys. 21, 1374 (1953); ibid 36, 2681 (1962).

[23] Kistiakowsky and Bradley, J. Chem. Phys. 35, 256 (1961); ibid 35, 264 (1961).

* For a review of the current state of the art concerning the oxygen fluorides see final report on contract NASr-38, Stanford Research Institute, Nov. 1, 1962.

B. Cryogenic Purification and Mass Spectrometer Inlet System

Every chemist is familiar with the bands of deposits that may be found in a cold trap on a vacuum rack when mixtures of substances are passed through. This effect is particularly noticeable when the dewar around the trap is only partially full of refrigerant (i.e., when there is a thermal gradient in the trap). The objective of the purification system being developed here is to control this gradient and to use it as a somewhat crude separative procedure. We have called this arrangement "thermal chromatography." In addition, the coldest end of the tube upon which the desired gradient is impressed is provided with a capillary leak such that the vapor in the cold end of the tube is bled into the ion source of a time-of-flight mass spectrometer. The physical arrangement is such that this vapor is in no way heated above the operating temperature of the cold end of the gradient tube before it is ionized in the electron beam of the ion source.

Since this system has already been described in detail,[19] only a brief outline is presented here for completeness. There is also included here some more recent operating characteristics of the cryogenic purification-inlet arrangement.

1. Brief Description

The inlet arrangement is schematically shown in Figure 3. Essentially one has two chambers connected by a copper tube 8 in. long and with a wall thickness of 0.100 in. designed to allow a maximum heat flux by conduction of 1000 cal/min when there is impressed a maximum gradient of 8° K/cm

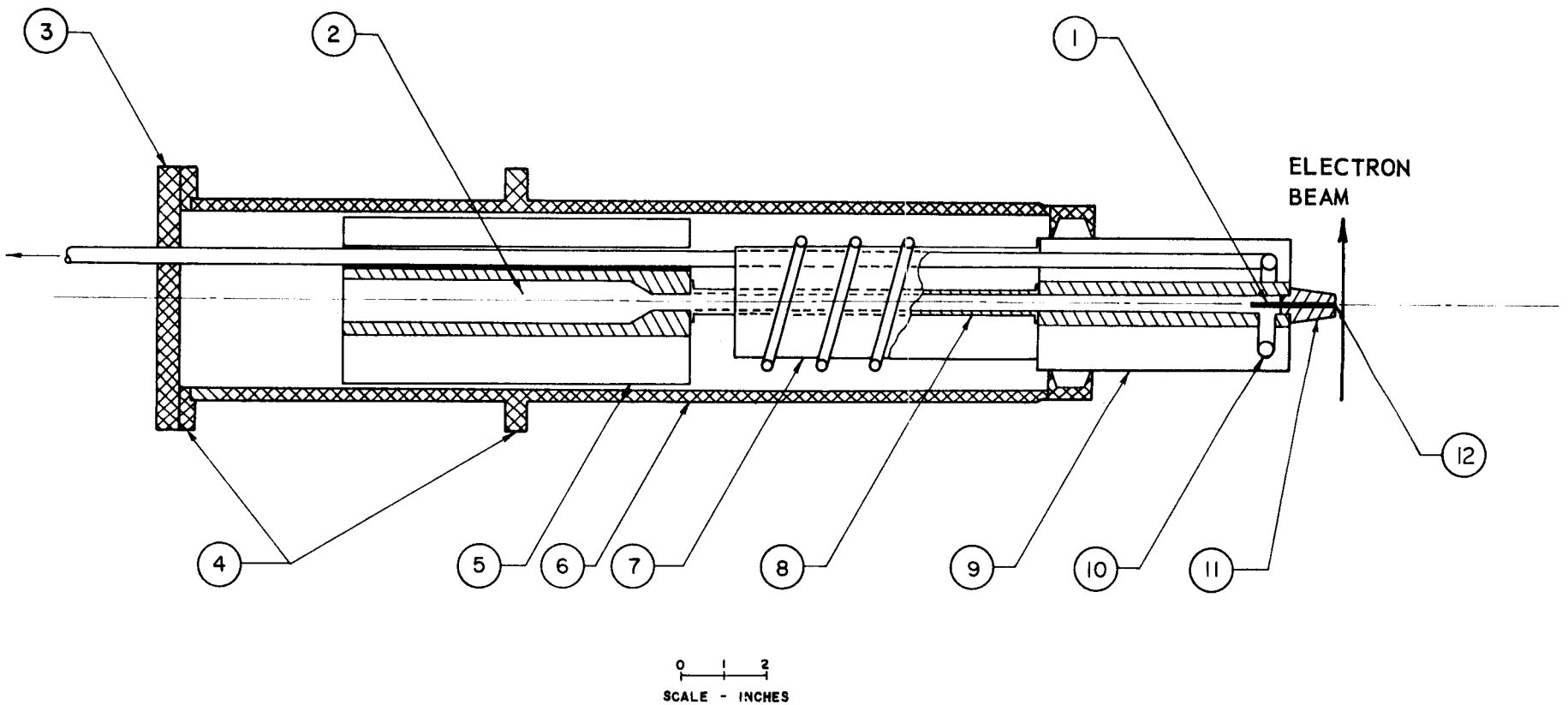

Figure 3. Schematic Diagram of Thermal Gradient Freeze-Out Assembly and Cryogenically Cooled Mass Spectrometer Sample Inlet System.

($k = 4.2$ watts/cm$^{\circ}$ K for copper[24]). This would correspond to the upper chamber being held at -33° C if the lower chamber is at nitrogen temperature. The maximum thermal load on the tube due to cooling and condensation of the species of interest was estimated to be 6 cal/min. This much energy being deposited over even a few mm of length in the gradient tube could hardly effect a thermal gradient that is moving 1000 cal/min. Of course, as the gradient is adjusted to less steep values, the 6 cal/min will represent more of a perturbation, but it will never be a significant one.

The temperature of each end of the gradient tube is separately regulated by injecting a controlled stream of liquid nitrogen into the end chambers. Minor variations are then compensated for by a heater wound on the center tube of each chamber. The power dissipated in each heater is controlled by a pair of Leeds and Northrup AZAR (adjustable zero, adjustable range) recorder-controllers, type 3-661-176-186-6-030-19, Speedomax H, Model S. The sensor is a single junction copper-constantan couple made of L & N wire No. 24-55-11 which was claimed by the manufacturer to be of unusually high accuracy.* Although it was felt that simple two position control on the bucking heater would be adequate, it seemed wise nonetheless to install controllers that were prewired for proportional control (basically a control slidewire on the main shaft of the instrument). Subsequent operation of the device has demonstrated the adequacy of the two position control except for the most precise applications, as will be discussed below.

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[24] The thermal conductivities at cryogenic temperatures of many materials is given by WADD Technical Report 60-56, Part II, A Compendium of the Properties of Materials at Low Temperatures, V. J. Johnson, general editor, Oct., 1960.

* $\pm$ 1/4° F for hot junction at 175° F and reference junction at 32° F, see L & N booklet EN-S2, 1963, p. 22.

The control microswitch on the AZAR's has a dead band of 0.2 per cent of scale length, which for a minimum span of 0.666 millivolts corresponds to switching action occurring upon a change of 1.3μvolt from the sensor. At 77° K this is equivalent to 0.08° K, at 273° K it is equivalent to 0.03° K, and varies more or less linearly at intermediate points.

Typical of the actual control that was obtained is to within maximum excursions from control of 2.5μvolt or $\pm$ 0.08° C for the high end at -96° C and, at the same time, maximum excursions of 5μvolt or $\pm$ 0.3° C for the low end at -192° C. In this experiment the gradient of $[-96-(-192)]/8$ or 12° K/in. could hardly be significantly affected by these variations, and hence this degree of control, i.e., generally within a few tenths of a degree, is taken to be quite satisfactory.

In many quenching experiments, it is not necessary to inject liquid N_2 into the upper refrigerant chamber, indeed it is usually just the opposite in that the upper chamber will more often than not require a steady heat input in order to maintain the desired gradient. With liquid N_2 into the low end chamber only, its temperature was -192° C and the upper end finally stabilized at -163° C, i.e., producing a gradient of 3.6° C/in. This is just the potential required to balance the natural heat influx to the upper chamber with the heat being conducted down the 8 in. long gradient tube. These conditions require 14 cc of liquid N_2/min into the low end chamber. Unless the heat input is increased, due perhaps to an active species generation process of some sort being installed in the large ID section of the upper chamber, it is necessary to heat this chamber to maintain gradients greater than about 3.6° C/in.

This bottoming out of the high end takes a long time if liquid is only injected into the low end chamber. The low end bottoms at -196° C after one-half hour, while the upper end is at -70° C after one hour, at -120° after two and one-half hours and at -163° C after five hours.*

The ionizing electron beam of the spectrometer moves from bottom to top as indicated on Figure 3 and is 5/16 in. wide in the plane of the paper by 1/16 in. thick perpendicular to the plane of the paper. Since the cold snout of the bottom end chamber is 1-1/16 in. long by 5/32 wide and since it is inserted directly into the grid stack of the spectrometer, it is clear that lateral positioning is of utmost importance. The clearance between the backing plate and the first ion grid of the source is only 0.239 in. Precise positioning is necessary if the inlet is to not ground out a grid or, worse, to bump or scrape the grids sufficiently hard to physically damage them. We also wish to position the outlet port on the center line of the electron beam, or, more properly, we wish to maximize the ion intensity. This was accomplished with a pair of diametrically opposed threaded push-rods provided with an O-ring seal which move in a fixture welded to the "cross" unit of the spectrometer. These

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* The fact that liquid N_2 was not usually needed in the upper end chamber was convenient in that a leak developed there which opened badly only when the chamber was cold. To continue working, this leak was not immediately searched out, but rather the refrigerant space was evacuated with an auxiliary mechanical pump. Under the conditions of the low end at -187° C and the upper end at -154° C, the pressure just upstream from the cold trap on the isolation space vacuum pump was 3.3×10^{-6}. This should be compared with a pressure of 2×10^{-6} when the valve connecting the pumps to the isolation vacuum space is closed. The pressure in the isolation space was always about 3×10^{-5} reflecting the leak from the refrigerant space which is held at 50μ or so by the auxiliary mechanical pump.

push-rods bear on the sides of the low end refrigerant chamber, have given absolutely no vacuum problems, and have proven to be very effective devices for positioning the refrigerated sample delivery snout within the grid stack. This lateral positioning is also aided by the illumination of the end of the snout by the excellently collimated beam of light from the filament. The collimation is produced by the five slits of the Fox type electron gun. A sharp boundary between the diffusively and directly illuminated regions of the snout was clearly visible, and the push-rods readily moved the snout in this beam. Since the advance of the inlet device can only be actually viewed end-on, it is not possible to get a visual feel for the depth of its penetration into the grid stack. However, the trap current is an excellent indicator of this since the ionizing electron beam is grounded to the snout when it is advanced too far. Experimentally, it has turned out that a 3/16 in. advance of the snout will cause a change from the initial onset of the diminution of the trap current to its complete disappearance. The mass spectrum itself also goes from the slightest noticeable diminution to almost complete disappearance over this same 3/16 in. advance.

C. Manipulative Techniques in Low Temperature Chemistry

Most of our manipulative experience with highly reactive systems at low temperatures still centers around work with ozone fluoride, O_3F_2. We have synthesized the substance a dozen or so times in high yield in a 2-1/4 in. I.D. glass reactor in which 2 cm copper disc electrodes are mounted 8 cm apart. The O_2;F_2 reactant mixture is admitted at a point roughly halfway between the electrodes. The optimum operating conditions are a pressure of 15 mm Hg and a potential of 2500 volts between the electrodes. The yield was very sensitive

to the O_2;F_2 reactant mixture ratio and is optimum when stoichiometric. Typical production rates and yields in our synthesis procedure are formation of 1.7 ml/hr with an overall yield of 74 per cent as calculated from the volume of liquid produced per mass of reactant exhausted from a 16.4 l. storage tank as determined by pressure decrease.

O_3F_2 decomposes to form O_2F_2 in daylight at 90° K. O_2F_2 is solid at 90° K and hence on standing in the collecting tip of the reactor, the red liquid that was originally formed will become pasty. This increasing pastiness of the product has caused many manipulative problems, not the least of which was the clogging of capillary pipets. Although these circumstances are disconcerting if one is only trying to handle O_3F_2, it is probably a blessing in disguise in the long run. It has forced us to develop manipulative procedures which are more general and which will be transferable to all other unstable, highly reactive substances at very low temperatures. O_3F_2 is not so atypical when compared to the expected product mixtures from other experiments now in progress.

1. Use of Fine Bore Pipets Filled by Capillary Attraction

Several tests were made with 100λ pipets (0.1 ml) which had a 1.0 mm ID and were 12 cm long. It was felt that the liquid O_3F_2 would rise in a capillary pipet of its own accord and not require a suction filling. It didn't. The surface tension of O_3F_2 is not sufficient to offset its density of 1.75 gm/ml at 90° K and produce a significant rise in a 1.0 mm capillary. The liquid would also not stay in the capillary once it was filled. Smaller ID's would have a better chance, but it will now be hard to pick up enough of the material, and also plugging will become a problem. This scheme was abandoned.

For transfer purposes the capillary pipet was held in a cylinder of pure lead (4 x 5/16 in) which has a high heat capacity at low temperatures. Once precooled, this would act as a "static" refrigerator for the sample pipet. This assembly was on the end of a rod so that it could be extended and retracted within a glass sleeve which had an evacuated annulus. The total assembly of the sample in the capillary pipet in the block of lead inside the sleeve shaped dewar could then be safely carried from the reactor to the spectrometer. This must be done rapidly, however.

2. Liquid Nitrogen Cooled Pipet Refrigerator

To avoid worries about the thermal capacity of the "static" arrangement and to allow a timewise more leasurily operation, the pipet cooler shown in Figure 4 was built. With liquid nitrogen in the reservoir, and with only room temperature radiation falling on the heavy copper tube, its bottom end would stabilize out at 85^{o} K according to design calculations. The design calculated total liquid loss rate was 1.1 ml/min, and it was subsequently measured to be 2.2 ml/min with an annular space pressure of 2×10^{-6}. The liquid capacity is such that the cooler will maintain its lowest temperature for 1 hour on one filling. A long pipet rides in the center through-hole. The operating sequence is as follows:

(a) The pipet in its cooler is inserted into the reactor. The tail of the cooler dips well below the refrigerant level around the cryogenic reactor.

(b) The pipet is extended deeper into the reactor, contacts the liquid, and a sample is withdrawn.

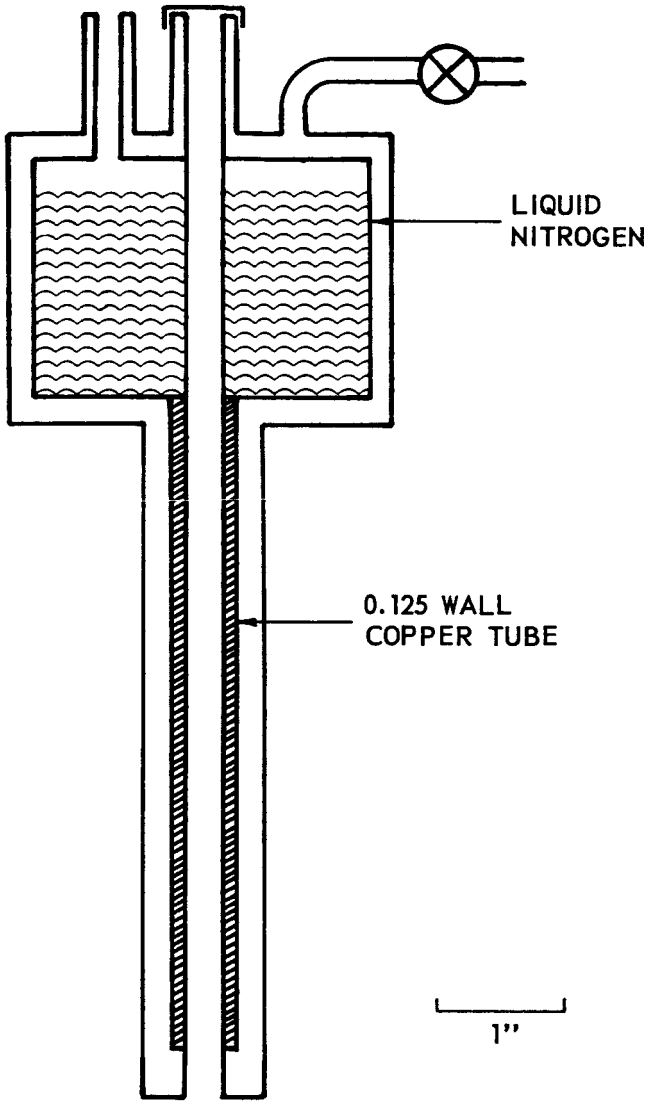

Figure 4. Schematic of Cooler for Transfer Pipet.

(c) The pipet is retracted into the cooler such that all of the sample is within the through-hole of the cooler and thus shielded against temperatures greater than about 80° K.

(d) The cooler, containing the completely retracted pipet is removed from the reactor and inserted into the precooled mass spectrometer inlet system.

(e) The pipet is again extended to a point down the gradient tube consistent with the gradient established therein and with the degree of separation that one is trying to effect. The sample is expelled from the pipet into the inlet system.

(f) The pipet and cooler assembly is withdrawn from the inlet system, and the analysis is carried forward.

While all of these operations are very simple at room temperature, they become most complicated when one is working with highly unstable substances about which very little is known and always deep inside a dewared arrangement. In none of these operations may the sample be warmed, sometimes not even slightly warmed. It is certainly true that one of the severest problem areas in our operations today is merely the translation of all of the normal manipulations of bench scale chemistry to operate at cryogenic temperatures.

D. Trapping of Species Generated by Pyrolysis

One of the most convenient ways to produce reactive molecules is by the pyrolysis of some suitable parent substance. The apparatus is simple, i.e., a furnace is easier to build and operate than is a gas discharge or a photolysis. Also, since the pyrolysis is milder than is, say a gas discharge, it will usually be possible to produce copious quantities of the species of

interest in an effluent that is relatively simple in its constituency. Whereas the gas discharge will produce general fragmentation, and all sorts of electronic, and vibrational excitations; it will usually be possible with a pyrolysis to break only a desired bond to produce directly the species of interest. One must still worry about subsequent reactions of the now fewer fragments with themselves and with the parent.

Under this NASA grant we are presently experimenting with several types of pyrolysis arrangements which are differentiated largely by their different operating temperatures.

1. Allotropic Forms of Sulphur

We have been interested for some time in the possible preparation of new modifications of sulphur by the use of processes involving cryogenic temperatures. It is an easy matter, by adjusting the temperature and pressure, to produce a vapor rich in either S_2, S_6, or S_8.[25] Many trapping experiments have been done with this system, the earliest apparently in 1918, and many more in the last few years.[8] A particularly significant study that was reported a few months ago was carried out at Moscow by Maltsev.[26] He was able to produce a greenish white deposit at -196° which on rapid warming (10°/sec or more) melted at -60° C. The new liquid was also highly volatile at this low temperature.

These phenomena were explained as arising from the presence of S_6 and S_8 straight chain molecules in the deposit although he had made no direct

[25] Tuller, W. N., ed., The Sulphur Data Book, McGraw-Hill, New York 1954.
[26] Maltsev, A. K., Russian Journal of Inorganic Chemistry, 8, 1559 (1963).

observation of these species. This represents the preparation of a previously unobserved form of sulphur in the condensed phase by a process utilizing a cryogenic quench.

Also, in recent studies, Meyer has been trapping various sulphur vapors, with and without matrix gases at temperatures between 4° and 77° K.[27] He finds the Russian results to be not reproducible and thinks their original parent material must have been impure. Meyer found it very hard to prepare pure allotropes because of their high reactivity even at low temperatures.

We have done only one experiment (quick and dirty type) which did show separation into bands on quenching and did show sublimation on warming. We are able to make no statements about the purity of the parent. It could have been very impure.

This sulphur problem is not being pursued with these grant funds, but it seemed relavent enough to briefly mention in this report.

2. Preparation and Properties of Diatomic Sodium

A second pyrolysis experiment, but one requiring much higher temperatures is being set up in the apparatus shown schematically in Figure 5, and is concerned with the isolation of diatomic sodium. Molecular sodium

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[27] Private communication from Dr. Beat Meyer, Lawrence Radiation Laboratory, University of California, February, 1964.

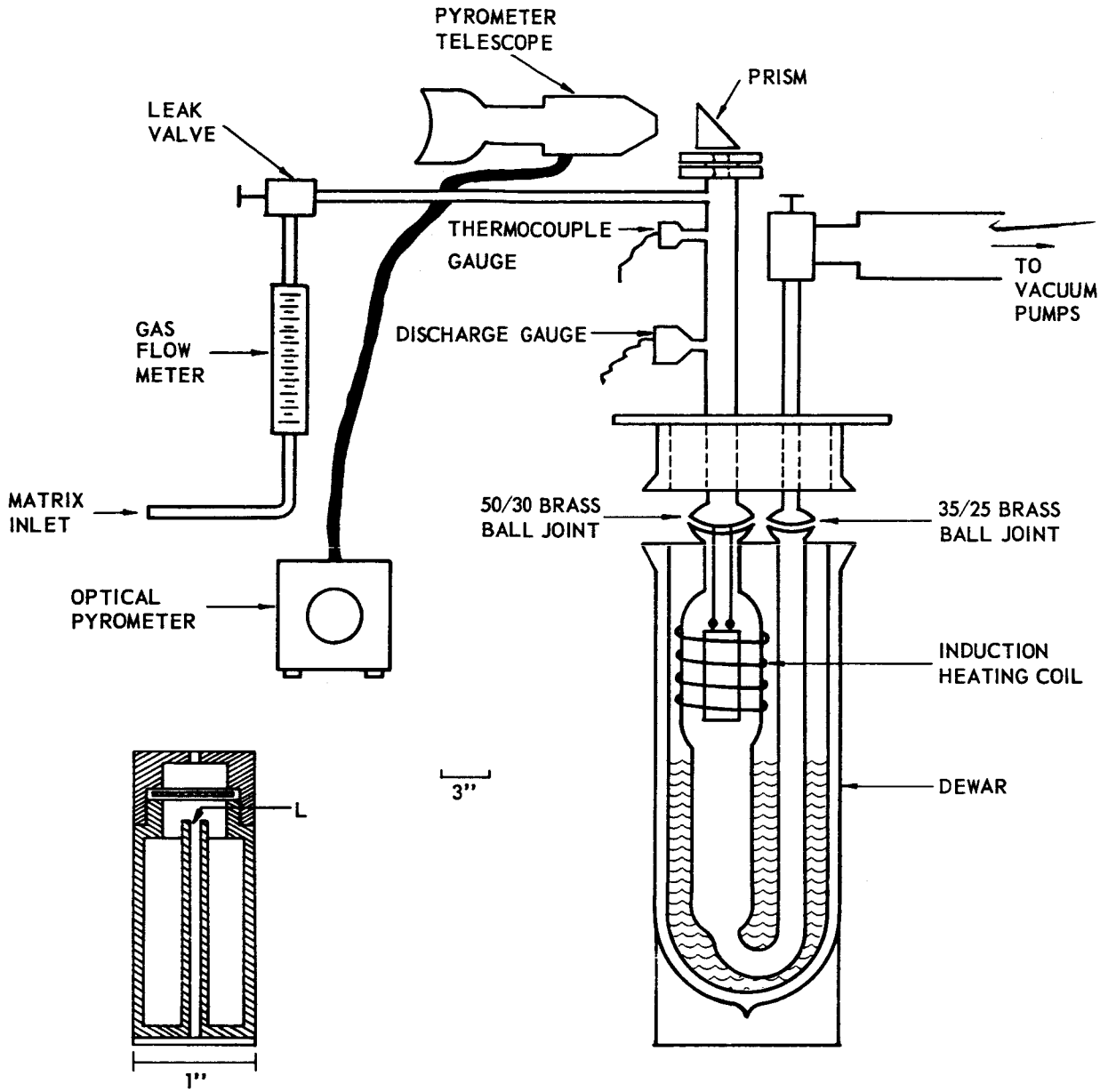

Figure 5. Schematic of Apparatus for Preparation of the Diatomic Alkali Metals with an Insert Showing More Detail of Cell.

exists in rather high concentration in the vapor over boiling liquid sodium. The construction of Na_2 as a function of temperature has been calculated using free energy data from Sittig[28] and the results are shown in Figure 6. At its normal boiling point of 883° C, the vapor is 17 mole per cent Na_2. The vaporization cell, shown in the insert of Figure 5, was fabricated from type 446 stainless steel and weighs 117.6 gms. This steel was selected for its high temperature resistance to molten sodium. One may not use copper, copper alloys, or nickel alloys with hot molten sodium.

The selected stainless steel, which was unfortunately very hard to machine, is essentially a chromium-iron alloy (23-27 per cent Cr) with 1 per cent or less each of C, Mn, Si, Ni, and N. The most corrosion resistant pure metals are molybdenum, niobium, tantalum, tungsten, and iron, and each of these represents a possible alternate material of construction for the cell.

The sodium is cut up, washed, dried and loaded into the cell in a glove box in an inert atmosphere of nitrogen.

In order to freeze out the sodium (both atomic and molecular) and its inert carrier, one must obviously remove from the composite gas stream, a certain amount of heat. For fixed operating conditions, the required rate of heat transfer will depend upon the total mass flow rate only. Because of the obvious limitations on the heat transfer to the liquid nitrogen in our U-tube arrangement, it was necessary to have a very slow flow of sodium out of the cell. Hence a hole of 0.0035 in. diameter was drilled in the

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[28] Sittig, Sodium-Its Manufacture, Properties, and Uses, Reinhold, New York, 1956; Handling and Uses of the Alkali Metals, Advances in Chemistry Series #19, American Chemical Society, Washington, D.C., 1957; Stainless Steel Handbook, Allegheny Ludlum Steel Corporation, Pittsburgh, 1959.

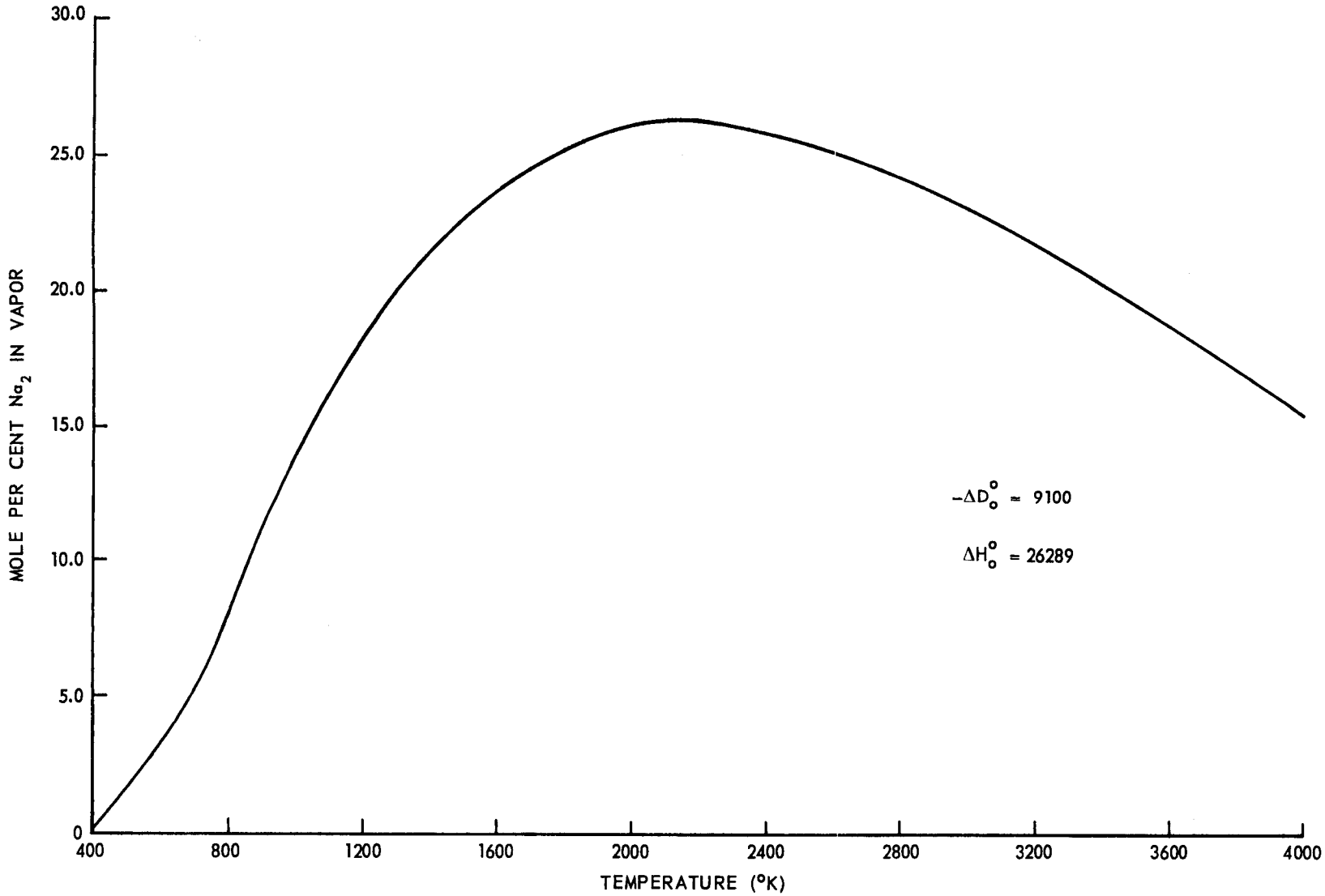

Figure 6. Calculated Concentration of Na_2 as a Function of Temperature in the Equilibrium Vapor over Boiling Liquid Sodium.

bottom of the re-entrant well of the cell at the point marked "L" on Figure 5. It is interesting from a mechanical fabrication point of view that this hole was drilled with a Vigor, stock number DR-560, flat type drill, using a jewelers drill press and a stero-microscope for observation of the operation.

According to our calculations, this leak, which has a characteristic ℓ/r (i.e., length over radius) of 6, will allow a mass flow of sodium of about 42 milligms/min which is within the heat transfer capability of the quenching arrangement.*

The selection of a matrix material for use in these experiments is difficult because of the extreme reactivity of the hot sodium vapor. We are presently concentrating on argon, which meets the requirements for inertness, but the solid does not have a low enough vapor pressure for ready utilization as a matrix at pumped nitrogen (63° K) or at pumped oxygen temperatures (54° K). The best available vapor pressure compilation on argon is that of Ziegler, et al[29] from which some selected points are given below.

T($^{\circ}$ K)	p(mm Hg)	
87.291	760	(n.b.p.)
83.80	516.84	(t.p.)
80.00	300.64	
77.00	188.74	
70.00	54.437	
65.00	18.913	
60.00	5.504	
55.00	1.272	

* Flow rate calculations from Knudsen cells, which is a similar problem to the present situation, are discussed by Carlson, et al, J. Chem. Phys. 38, 2725 (1963).

29 Ziegler, Mullins and Kirk, Georgia Tech Research Institute, Technical Report No. 2 on contract CST-7238, NBS, Boulder, Colorado, Calculation of the Vapor Pressure and Heats of Vaporization and Sublimation of Liquids and Solids, Especially Below One Atmosphere. II Argon, June 15, 1962.

T($^{\circ}$ K)	p(mm Hg)
50.00	0.218
40.00	1.68×10^{-3}
30.00	4.95×10^{-7}
20.00	4.54×10^{-14}

Hence, it may be necessary to use liquid hydrogen as the refrigerant, or to go to a lower vapor pressure matrix.

We expect the forces between Na atoms to be greater than that between sodium molecules and hence the atomic form should freeze out first in the U-tube trap. It is also not important that the atomic form be co-condensed with a matrix. However, it is important that the Na_2 be so co-condensed, for we wish to subsequently pump away the matrix and thus allow the trapped Na_2 molecules to come together with energies near 3/2 kT with T equal to say 60° K and not 600° K.

E. Reactivity of Atomic Hydrogen

It has again seemed wise to carry out experiments on a rather macroscopic scale in glass where phenomena may be visually noted. We are interested in contacting crystalline and glassy materials, and more particularly in contracting liquid reactants with atomic hydrogen.

Of the many possible reactor configurations for contacting a gas with a liquid, we have chosen the simplest, i.e., a simple jet of gas onto the free surface of a briskly stirred pool of the liquid phase. This is to be accomplished in the apparatus shown schematically in Figure 7. This arrangement is currently undergoing vacuum leak tests.

It is clear that the discharge must be operated at pressures higher than the vapor pressure of the liquid phase. Indeed it would be desirable to have

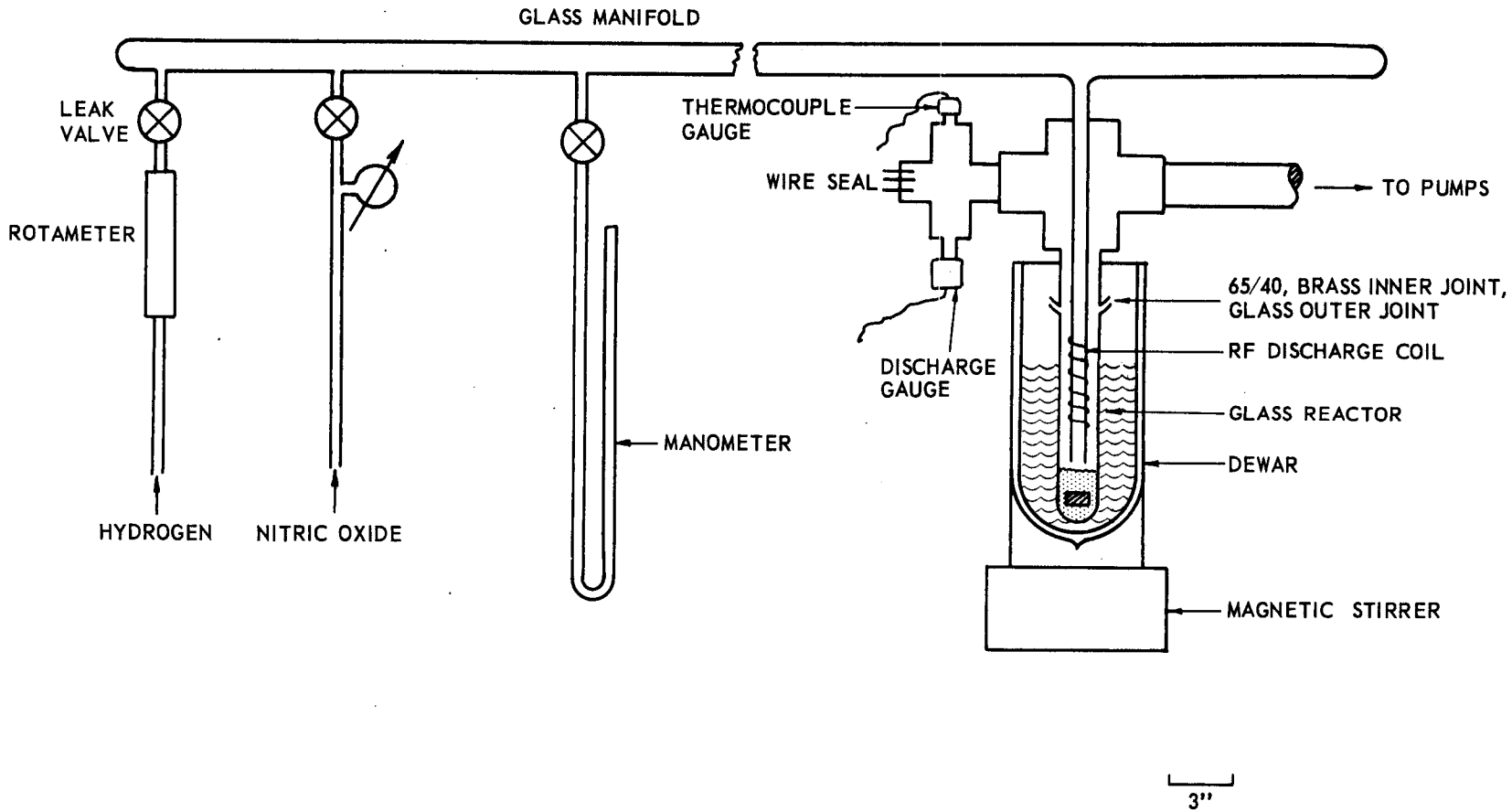

Figure 7. Schematic of Apparatus for Hydrogen Atom Reactivity Studies.

a zero vapor pressure liquid phase so that reaction would occur between species in the liquid phase. Of course, there is no zero vapor pressure liquid so that the observed reactions could be occurring in the liquid, in the liquid-vapor interfacial region, or in the vapor phase. It will be possible to differentiate between all of these experimentally, however. For example, the reaction of only the cold vapor of the normally liquid reactant could be observed. The liquid reactant could also be dissolved in some lower vapor pressure solvent. It is noteworthy that a search of only the routine reference sources, i.e., a reasonably thorough, but not complete search, led to lists of 108 organic and 34 inorganic substances that have freezing points below 150° K. So there are many more possible solvents for use in low temperature chemistry than one might have supposed.

Power for the gas discharge is provided by a type BC-610 military transmitter that was obtained on surplus at essentially zero cost.* This power supply gives up to 1 KW at any frequency between 2 and 18 mc.

The first series of experiments in this apparatus involve atomic hydrogen reacting with liquid nitric oxide, NO. The freezing point of NO is 110° K, where it has a vapor pressure of 178 mm Hg. We are interested here in the possible free existance of HNO at these sorts of temperatures. Such existence of this species has already been postulated as resulting from somewhat similar experiments performed in 1933. These very early experiments are interesting, but definitive measurements or identification of materials at the low temperatures was never performed, indeed, it was impossible with the then available instrumentation.

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* There had been a $1000 equipment allotment in the budget for this power supply. This money was subsequently used for a digital voltmeter which was not mentioned in the budget.

F. Krypton Fluorides

We have used a reactor very much like that described for the O_3F_2 synthesis, to synthesize several fluorides and oxyfluorides of the "inert" gas krypton. Our arrangement and procedure was very much like that described a few months ago by Grosse.[30] The mixed elements are slowly pumped through a discharge tube reactor made of pyrex glass which is immersed in liquid oxygen. After an hour or so, the reaction is stopped and the reactor removed from the liquid oxygen and immersed in a dry ice-alcohol mush (-78° C). All species that are volatile at this temperature, principally SiF_4, are pumped away. The solid remaining in the reactor is then sublimed into a transfer trap for connection to the mass spectrometer inlet system. The results of this experiment are most difficult to reproduce. Our best successes have been in reproducing only the absence of any measurable reaction. However, in one of the more happy experiments, the following mass peaks were observed and the indicated assignments were made.

Mass	Ion	Mass	Ion
47	SiF	117	KrOF
66	SiF_2	129*	I
84	Kr	134	$KrOF_2$
85	SiF_3	149*	C_2I
99	KrF	150*	C_2I
103	KrF	160	KrF_4
104	SiF_4	178	KrF_5
114	KrOF	197	KrF_6

* These peaks arise from incomplete pump-out of spectrometer from preceding analyses.

[30] Grosse, et al, Science 139, 1047 (1963).

This spectrum, which is our best effort to date, was really not very good so that there is some uncertainty in the mass assignments.

In view of the apparent instability of these species, the best way to do this experiment would be to mount the discharge electrodes in the enlarged section of the upper end refrigerant chamber of the gradient-inlet apparatus (see Chapter II, B). This would avoid any need for warming the product in the vapor phase to room temperature. In the transfer and inlet arrangement used above, an effort was made to minimize the time during which the vapor passed through a tube at room temperature, but perhaps the decomposition of the molecule is too fast for this technique. An equally probable difficulty is that the conditions in the reactor leading to the formation of the krypton compounds are very critical.

Our data, though rather poor and only partially reproduciable, do indicate that the fluorides KrF_2, KrF_4, KrF_6 and the oxyfluoride $KrOF_2$ exist. The results obtained here are probably the most definitive on the question of the existence of these molecules that have been reported to date.[31] The molecules are analogous to the corresponding and now well known xenon compounds.

This work was done as a special problem, and we have no immediate plans for continuing studies on the nobel gas compounds. Several more attempts to reproduce the data above will be made before publishing these results.

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[31] A good introduction to this very new and interesting field is found in Nobel Gas Compounds, Hyman, ed., University of Chicago Press, in press. This book contains the proceedings of a conference held at Argonne National Laboratory on this subject in April, 1963.

III. PLANS FOR NEXT REPORTING PERIOD

During the next six months, the principle vectors of this research program should shape up about as follows:

a) Continue to develop operating characteristics of the cryogenic purification and inlet system using O_2F_2 and O_3F_2 mixtures.

b) Develop appearance potentials and ionization potentials of species from these oxyfluorides along lines discussed in Chapter II, Section A, hopefully leading to a better understanding of the structure and bond energies of these substances.

> COMMENT: Now admittedly these species are of relatively little interest in developing knowledge directly applicable to the chemistry of comets and planetary atmospheres. Its relevance here is that it provides an excellent vehicle for the continued development of our cryogenic purification and inlet system. The best successes of this NASA program do depend completely on this inlet operating according to design. In addition, and as a by-product, the study of the oxyfluorides is very interesting in its own right.

c) Complete the preliminary check-outs and initiate work with the reaction of atomic hydrogen with NO, both with the pure liquid and in solution.

d) Perform a series of quenching experiments with sodium looking for the trapping of Na_2 in its $^1\Sigma$, i.e., molecular ground state.

> COMMENT: Both of the experimental set-ups for these studies are essentially ready. The sodium apparatus only lacks installation of the induction heating system and the H atom apparatus is now getting vacuum tests.

In addition to these continuation experiments that are in many ways obvious from the present status of the research as background, several significant expansions in scope are being discussed and will hopefully soon be in full swing.

Some members of the staff of the diffraction laboratory are interested in determining the structures of some of the unusual molecules synthesized in this

work. A gonimeter equipped for use with a crystal maintained at liquid nitrogen temperature is on hand and in operation. The initiation of a continuing interplay between our synthesis and reactivity studies and these structure studies seems imminent.

One of our theoreticians has indicated some interest in trying to apply self consistent field, linear combination of atomic orbitals (SCF-LCAO) notions to these small molecules. It appears that for small molecules one can make predictions from theory about their expected chemical behavior with some degree of confidence. This then would represent a new area, i.e., close interplay between theoretical chemistry and experimental chemistry in situations where one can make optimum arguments from both sides. The theory can suggest further experiments and the results of these experiments can further improve the theory. This line of work could be very exciting.

IV. STUDENT PARTICIPATION

The research being done under this grant has been arranged such that each section forms the PhD thesis research of a graduate student in chemical engineering. There are now four graduate students working essentially full time on the research program of this grant on this basis. Each student holds a fellowship and these grant funds are used to supplement his stipend up to an allowed maximum of $1000 per year. Two of these students are National Science Foundation Predoctoral Fellows.